3,6-Bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazine: A Versatile Bifunctional Building Block for the Synthesis of Linear Oligoheterocycles

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Dedicated to Professor Sho Ito on the occasion of his 77th birthday

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3,6-Bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazine (**3**) (BTT) is an energy-rich compound and a strong dibasic acid. The bifunctional compound **3** is capable of [4+2] cycloadditions through its tetrazine unit as a 4π compound, and of acylating ring-opening reactions through its tetrazole rings, leading to the formation of linear oligoheterocycles **7**, **12** with 1,2,4,5-tetrazine, pyridazine, 1,3,4-oxadiazole, thiophene, furan, and pyrrole units in sequences not easily available by other synthetic methods.

Introduction

Supramolecular chemistry is a rapidly expanding field at the frontiers of chemical science, overlapping with physical and biological phenomena.[1−7] In essence, it concerns the self-assembly of smaller molecules to form larger entities with interesting properties. Energy-transfer phenomena, electron-conducting devices, molecular wires, molecular machines, supramolecular metallocatalysis, and material science are all fields of active investigation, to name but a few examples.

Invariably, the goal of synthesis is to allow access to new building blocks, which, through non-covalent interactions, hydrogen bonding, or metal complexation, subsequently form larger units in a well-defined manner, ultimately leading to supramolecular systems with new properties.

Frequently used building units are bipyridines[8] and terpyridines,[9] but the use of "mixed" combinations such as pyridine-pyridazine,[10] pyridine-pyrimidine,[11] pyridine-pyrazine,[12] pyridine-1,3,5-triazine,[13] and pyridine-1,2,4,5-tetrazine,[14,15] has also been reported in the literature. Furthermore, the properties of the building blocks and supramolecular structures can be varied by introducing combinations with five-membered heterocycles into the chains, e.g. with thiophenes, pyrroles, furans, 1,3,4-oxadiazoles, or 1,3,4-thiadiazoles.[16,17]

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In this contribution, we report on a synthetic route to heterocyclic chains with alternating five- and six-membered heterocycles using 3,6-bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazine (**3**) (BTT).[18]

Results and Discussion

Recently, we obtained access to linear, branched, and superbranched oligopyridines and metal complexes thereof by a rather simple reaction path using the novel "LEGO" system.[19] We have since sought another facile access to redox-active linear oligoheterocycles that would allow modification of the chain in a straightforward manner. For this purpose, we have used BTT (**3**) as a building block, which may be modified by [4+2] cycloadditions and ring transformations.

BTT (**3**) was first synthesized in a pure state as early as 1915 by Curtius,[18b] who disproved earlier structural proposals by Lifschitz.[18a,18c,18d] No definite reactions of **3** besides formation of a sodium salt and hydrolytic ring-opening of the central 1,2,4,5-tetrazine unit have since been reported.[18]

We followed the Curtius protocol (Scheme 1) and isolated the dihydrotetrazine **2** as yellow crystals, melting at 237−238 °C with decomposition. BTT (**3**) forms carmine-red crystals, which can be used directly as obtained after the oxidation step (Scheme 1). Purification by recrystallization from ethanol, as recommended in the literature,[18b] did not improve the purity in our hands, probably because the high oxidation potential of BTT (**3**)[20] is responsible for a redox reaction with ethanol to form **2** as an impurity.

Curtius reported[18b] that **3** can be handled without special precautions. In contrast, we found BTT (**3**) to explode violently above 220 °C depending on the heating rate. Dif-

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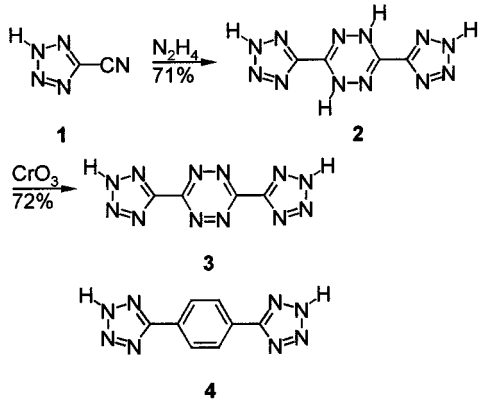
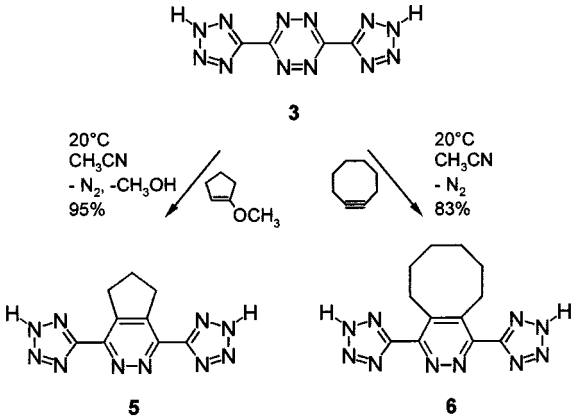


Scheme 1. Synthesis of BTT (**3**)

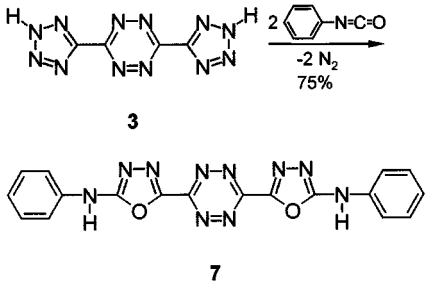
ferential scanning calorimetry (DSC) measurements proved that the thermal decomposition of BTT (**3**) occurs violently within a very narrow temperature range of a few degrees Celsius, starting at about 231 °C with a maximum at about 236 °C. The heat of decomposition was measured as 533 kJ/mol, about four times the value of the common explosive 2,4,6-trinitrotoluene (TNT). The heat of decomposition of 1,4-bis(2*H*-tetrazol-5-yl)benzene (BTB) (**4**)[21] is also quite high (255 kJ/mol). Therefore, both BTB (**4**) and BTT (**3**) should be handled with care. A special warning for the use of **3** in particular is given in the experimental section.

BTT (**3**) is a strong dibasic acid, the neutralization curve with 0.05 M NaOH solution as titrating agent showing only one inflection point at pH 6.86, corresponding to the neutralization of two protons. The pH value of solutions of BTT (**3**) in distilled water indicates that one proton is almost completely dissociated. Unfortunately, we could not measure exact pK_a values because BTT (**3**) decomposes quite rapidly in both basic and acidic aqueous solutions. The high acidity of BTT (**3**) also precludes its use in [4+2] cycloadditions with acid-sensitive dienophiles, such as enamines and ynamines. Furthermore, the acylating ring-opening reaction cannot be performed in pyridine solution because BTT (**3**) forms stable bis(pyridinium) salts.

According to kinetic measurements,[20] BTT (**3**) is a highly reactive diene in inverse-type Diels–Alder reactions, almost approaching 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine in its reactivity.[15] An orange solution of BTT (**3**) in acetonitrile at 20 °C was discoloured within a few minutes following addition of the highly reactive cyclooctyne (Scheme 2).[22] The pyridazine derivative **6** could be isolated in high yield in a pure state. 1-Methoxycyclopentene is almost 10^6 times less reactive than cyclooctyne,[22] hence the cycloaddition product **5** was obtained only after ten days at ambient temperature in acetonitrile (95%). **5** is formed through a sequence of [4+2] cycloaddition, cycloelimination with loss of molecular nitrogen, followed by β-elimination of methanol.



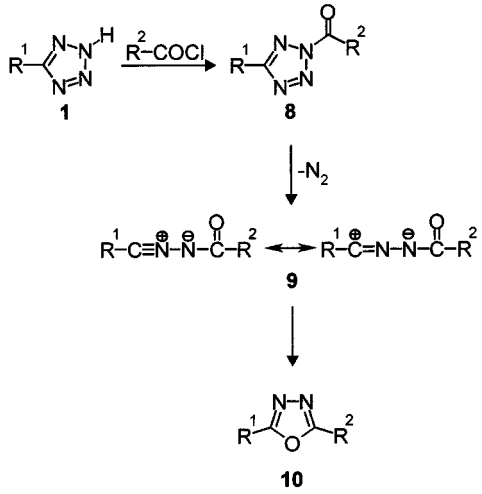
Scheme 2. [4+2] Cycloaddition reactions of BTT (**3**)



Scheme 3. Acylating ring-opening of BTT (**3**) with phenyl isocyanate

Phenyl isocyanate proved to be the only acylating agent with cumulative double bonds that could be successfully employed. When a suspension of BTT (**3**) in the heterocumulene was heated to reflux, evolution of two equivalents of nitrogen was observed; the orange bis(oxadiazolo) tetrazine **7** could be isolated after recrystallization from *N,N*-dimethylformamide in 75% yield (Scheme 3). Unfortunately, all attempts to perform analogous reactions with phenyl isothiocyanate or dicyclohexyl carbodiimide were unsuccessful. No definite products could be isolated. Carboxylic acid imide chlorides likewise failed as acylating agents.

The acylating ring-opening of tetrazoles is a well-known standard procedure for the synthesis of 1,3,4-oxadiazoles under mild conditions.[17,23–25] Ring-opening and sub-



Scheme 4. Acylating ring-opening of 5-substituted tetrazoles **1** to give 1,3,4-oxadiazoles **10**

sequent dinitrogen loss from the intermediate 2-acylated tetrazoles **8** leads to *N*-acylnitrilimines **9**, which undergo ring-closure to 1,3,4-oxadiazoles **10** (Scheme 4). The intermediacy of the 1-acylated isomers prior to formation of 2-acylated tetrazoles **8** has also been postulated in the literature. In this communication, for simplicity, we prefer to formulate the 2-acylated tetrazoles, which are finally transformed to the oxadiazoles according to Scheme 4.

The bifunctional BTT (**3**) is amenable to the formation of linear oligoheterocycles with alternating heterocyclic units (Scheme 5).

Thus, BTT (**3**) reacts with two equivalents of an aliphatic, aromatic, or heteroaromatic acyl chloride **11** to form the 5-substituted 3,6-bis(1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazines **12** (Scheme 5, Table 1). Depending on the acid chloride used, symmetrical heterocyclic chains with up to five heterocyclic units are readily accessible.

The 3,6-bis(1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazine (**12i**) could be formed by two different routes, either in direct analogy to Scheme 5 by heating **3** with acetic anhydride under reflux, or by the two-step reaction according to Scheme 6 using acetyl chloride as the acylating agent. The isolation of *N*-acetylated BTT (**13**) confirmed the mechanism of the acylating ring-opening of 5-substituted tetrazoles shown in Scheme 4. At present, we cannot offer unambiguous proof of the structure of **13** (1- or 2-acylated tetrazole). Heating of **13** in 1,2-dichlorobenzene at 160 °C led to the identical product **12i**.

The reaction of BTT (**3**) with *N*-methylpyrrole-2-carbonyl chloride (**11m**) failed because **11m** decomposes under the conditions used; however, the reaction of BTB (**4**) with **11m** succeeded (Table 2)

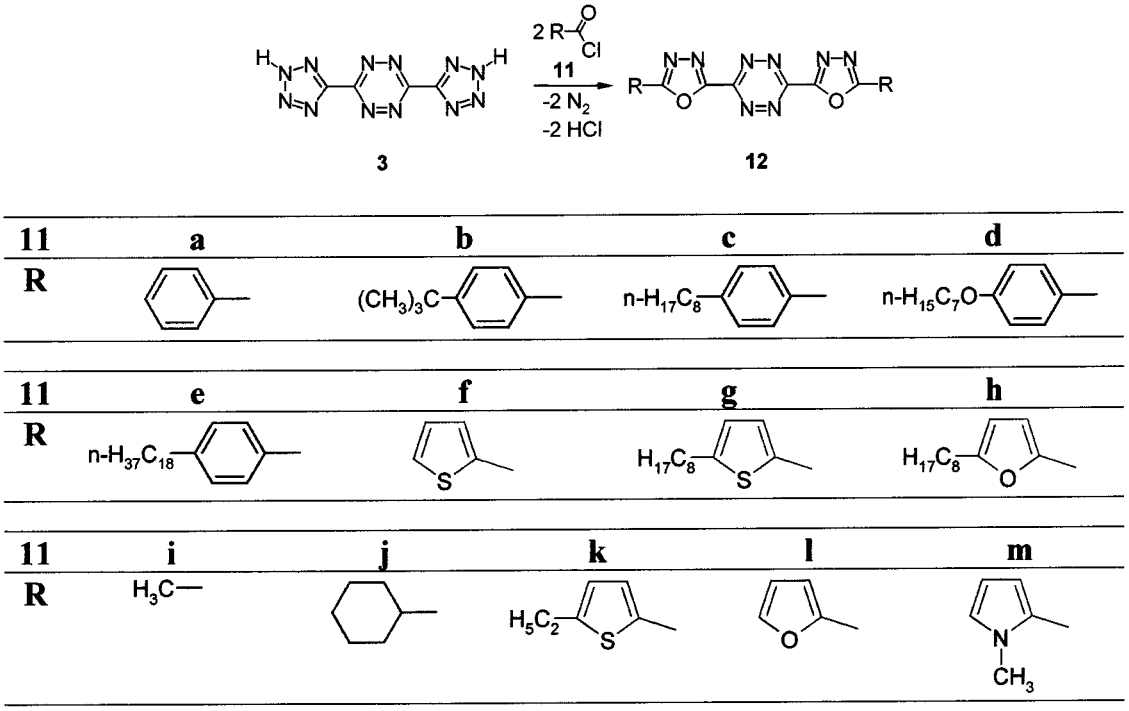
BTB (**4**) reacts in the same manner as BTT (**3**), but in pyridine solution, which allows reactions to be carried out at lower temperatures (Scheme 7, Table 2).

A further ring transformation could be achieved by [4+2] cycloaddition of the 1,2,4,5-tetrazine **12e** as a diene with norborna-2,5-diene as an angle-strained dienophile, which furnished the pyridazine **15** (Scheme 8). Norborna-2,5-diene acts as a synthetic equivalent of gaseous acetylene, which itself is too unreactive.[19,20]

One of the aims of this investigation was to achieve liquid crystal behaviour that showed a dependence on the length of the alkyl side chains and on the nature of the central aromatic rings. Unfortunately, with the exception of **12e**, all the 1,2,4,5-tetrazines **12** were found to decompose to some extent at their melting points. The melting peak of the second cycle was smaller and appeared at a lower temperature compared to the first one.

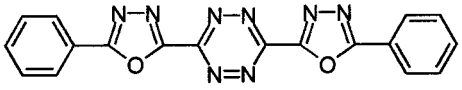
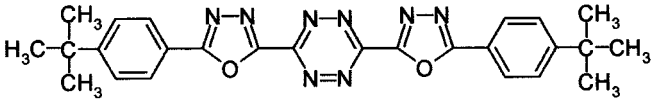
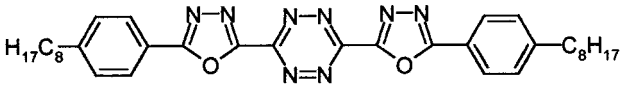
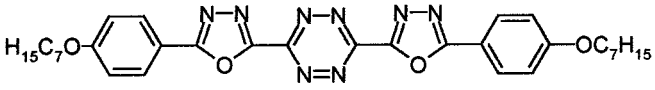
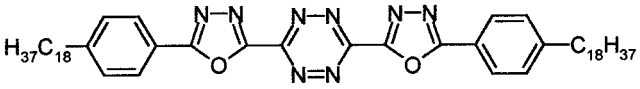
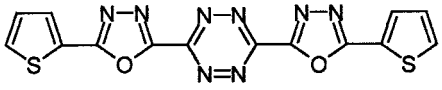
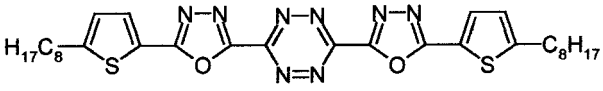
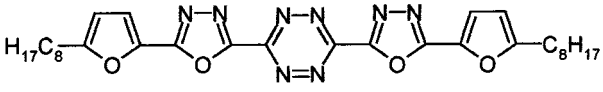
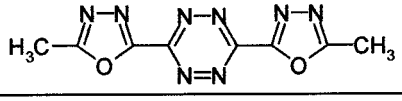
In contrast, the 4-octadecylphenyl derivative **12e**, which has the lowest melting point of all the tetrazines **12**, shows a liquid crystal phase between 146 °C and 173 °C according to DSC measurements. Moreover, little decomposition could be detected. Further experiments in this field would seem to be worthwhile as tetrazine derivatives have, in principle, indeed been shown to be compounds with liquid crystal properties.[15] To avoid decomposition of the 1,2,4,5-tetrazine derivatives **12** and pyridazine derivative **15**, the alkyl chains will probably have to be branched and/or extended, so as to give even lower melting points.

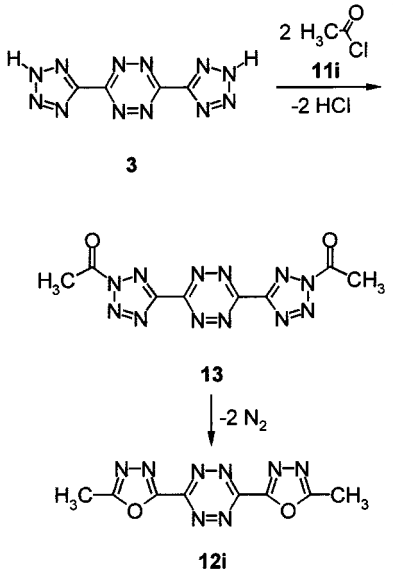
The coloured tetrazine derivatives **12** listed in Table 1 all show the expected nπ* absorption at around 520 nm, with ε values between 550 and 620 [$Lmol^{-1}cm^{-1}$]. The tetrazine ring as well as the oxadiazole unit are strongly electron-



Scheme 5. Reaction of BTT (**3**) with acyl chlorides **11** to give 3,6-bis(1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazines **12**

Table 1. 3,6-Bis(1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazines **12** synthesized according to Scheme 5

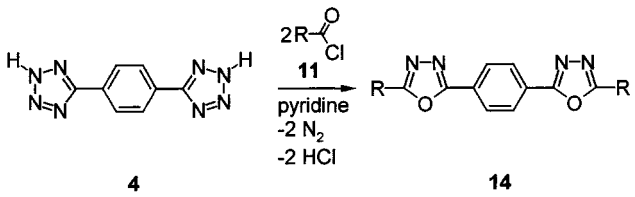
Acyl halide	Product		Yield [%]	*M.P.* [°C]
11a	**12a**		83	>280
11b	**12b**		74	265-267
11c[29]	**12c**		52	182-184
11d	**12d**		77	238-242
11e	**12e**		18	144-146
11f	**12f**		74	278-280
11g[30]	**12g**		41	177-179
11h	**12h**		11	162-164
11i	**12i**		82	243-245



Scheme 6. Stepwise reaction of BTT (**3**) with acetyl chloride (**11i**) to give 3,6-bis(1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazine **12i**

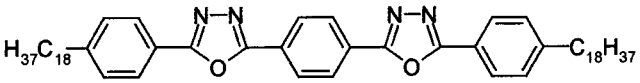
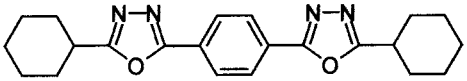
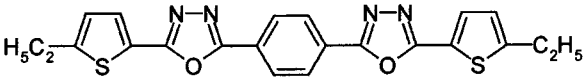
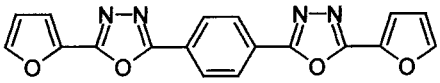
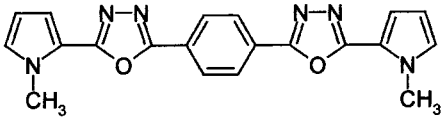
attracting substituents.[15,20] Therefore, the conjugation with donor substituents shifts the $\pi\pi^*$ absorption to longer wavelengths. Figure 1 shows this effect for the couples **12c**/**12d** (361 cf. 389 nm) and **12c**/**12g** (361 cf. 399 and 402 nm).

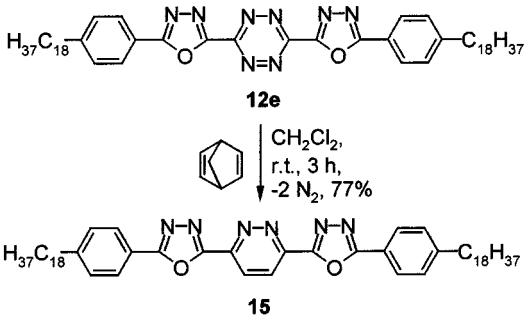
We also measured the half-wave reduction potentials for the tetrazines **12** (Table 1; reference electrode $Ag/AgNO_3$, 0.1 N Pr_4NBF_4). Within the limits of experimental error, we found $E_{1/2} = -0.76$ V for all the tetrazines, a value which is close to that for 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine ($E_{1/2} = -0.83$ V), a rather electron poor and reactive tetrazine in inverse type [4+2] cycloadditions.[15].



Scheme 7. Reaction of BTB (**4**) with acyl chlorides (**11**) to give 1,4-bis(1,3,4-oxadiazol-2-yl)benzenes **14**

Table 2. 3,6-Bis(1,3,4-oxadiazol-2-yl)benzenes **14** synthesized according to Scheme 7

Acyl halide	Product		Yield [%]	*M.P.* [°C]
11e	**14a**		86	210-214
11j	**14b**		22	209-211
11k[30]	**14c**		90	238-239
11l	**14d**		87	249-253
11m[31]	**14e**		73	264-266



Scheme 8. [4+2] Cycloaddition of **12e** with norborna-2,5-diene to give 3,6-bis(1,3,4-oxadiazol-2-yl)pyridazine **15**

Conclusion

BTT (**3**) and, as demonstrated previously, BTB (**4**)[23,24,25] are useful building blocks for the synthesis of heterocyclic chains with redox-active heterocycles. We have demonstrated the synthetic principle for oligoheterocycles up to five units. More diverse modification of the acid chlorides **11** used in the acylating ring-opening of the tetrazole units facilitates greater flexibility in the synthesis of the oligoheterocycles. The quest for molecules with liquid crystal properties looks very promising. Recently, 1,3,4-oxadiazole units have been the subject of numerous investigations, for instance, with regard to 1,3,4-oxadiazole-containing dendri-

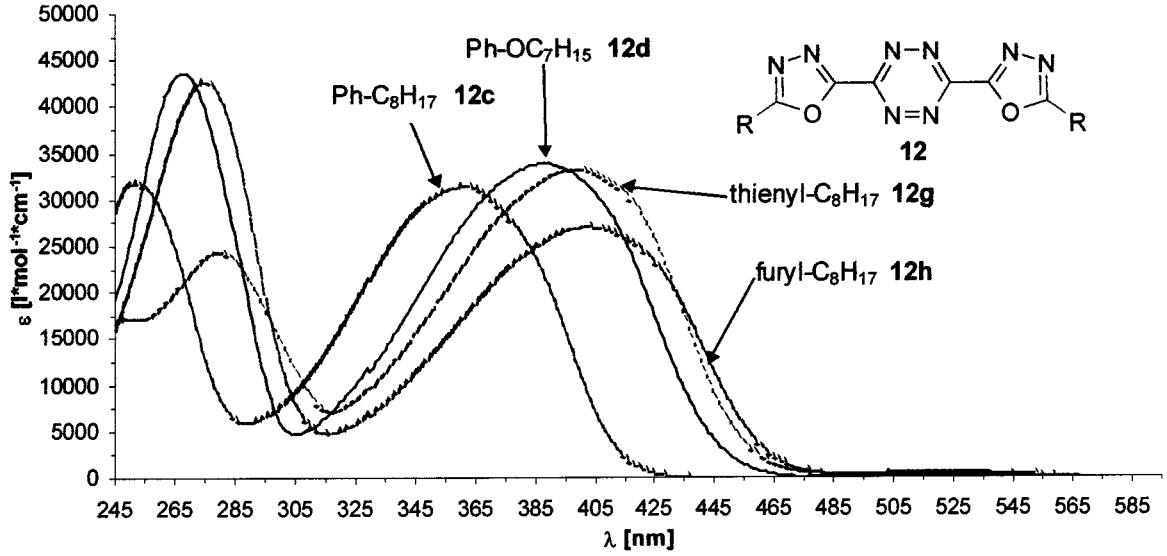


Figure 1. UV/vis spectra of 3,6-bis(1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazines **12** in CH_2Cl_2

mers,[17d] light-emitting molecules in combination with rhenium or ruthenium bipyridine complexes,[17b] or aromatic poly(1,3,4-oxadiazole)s[17c] as advanced materials.

In spite of the high energy contents of **3** and **4**, their use in synthesis does not present a problem as long as the necessary safety rules are obeyed (see experimental section).

Experimental Section

General Remarks: IR spectra were recorded with a Beckman Acculab I. − NMR spectra were obtained with Bruker AC250 and ARX400 spectrometers (250 MHz/400 MHz for ^{1}H and 63 MHz/100 MHz for ^{13}C). The degree of substitution at the C atoms was determined by the DEPT-135 method. − Mass spectra were recorded either by electron impact with an ionizing voltage of 70 eV on a Varian CH90 instrument or by field desorption or secondary ion bombardment (Cs^+) on a Varian MAT 311A instrument. − Melting points were determined either with a Büchi melting point apparatus (<280 °C) or with a copper block (>280 °C) and are uncorrected. − Elemental analyses were performed in the microanalytical laboratory of the University of Regensburg. − For analytical thin-layer chromatography, precoated plastic sheets (POLYGRAM SIL G/UV$_{254}$, Macherey−Nagel) were used. − Silica gel 60 (particle size 0.040−0.063 mm, Merck) was used for flash column chromatography (fcc). − Cycloaddition reactions were carried out under an atmosphere of argon in solvents dried according to standard procedures. − UV/vis spectra were recorded with a Karl Zeiss Specord M500 spectrophotometer. − Cyclic voltammetry was carried out with a voltage scan generator (Bank Wenking VSG 72), a potentiostat (Metrawatt Lerrayer XY 733), an Ag/0.1 N $AgNO_3$ reference electrode, and a Hg electrode, with 0.1 N tetra-*n*-propylammonium tetrafluoroborate in acetonitrile as the supporting electrolyte. − Differential scanning calorimetry was performed with either a TA Instruments MDSC 2920 or a Perkin−Elmer DSC7 with samples in open cubes.

Phenyl isocyanate, cyclohexanecarbonyl chloride (**11j**), benzoyl chloride (**11a**), 4-*tert*-butylbenzoyl chloride (**11b**), thiophene-2-carbonyl chloride (**11f**), furan-2-carbonyl chloride (**11l**), acetyl chloride (**11i**), acetic anhydride, and norborna-2,5-diene were purchased from Aldrich, 4-*n*-heptyloxybenzoyl chloride (**11d**) from Lancaster, and were used as received. 1,4-Bis(2*H*-tetrazol-5-yl)benzene (**4**) (BTB),[23] 5-cyanotetrazole (**7**),[26] cyclooctyne,[27] 1-methoxycyclopentene,[28] 4-octylbenzoyl chloride (**11c**),[29] 5-ethyl- and 5-octylthiophene-2-carbonyl chlorides (**11k**) and (**11g**),[30] and *N*-methylpyrrole-2-carbonyl chloride (**11m**)[31] were prepared according to literature procedures. 4-Octadecylbenzoyl chloride was prepared from 4-octadecylbenzoic acid[32] by treatment with thionyl chloride.

3,6-Bis(2*H*-tetrazol-5-yl)-1,4-dihydro-1,2,4,5-tetrazine Dihydrate (2): To a solution of 5-cyanotetrazole (**7**)[26] (6.02 g, 63.3 mmol) in dry ethanol (65 mL) cooled in an ice bath was added hydrazine hydrate (100%) (6.15 mL, 6.30 g, 127 mmol). After a few min., a colourless precipitate was formed, which turned yellow on heating under reflux for 15 min. (in contrast to the original literature report,[18b] the colourless precipitate was not separated). After refluxing for 2 h, further hydrazine hydrate (100%) (6.15 mL, 6.30 g, 127 mmol) was added and heating was continued for 22 h. The yellow precipitate was then collected by suction filtration, washed with ethanol (50 mL), and dried in vacuo over P_2O_5 at room temp. The yellow bis(hydrazinium) salt of **2** was dissolved in hot (85 °C) water (200 mL) and purified by hot filtration. The clear orange solution was cooled to 0 °C and concentrated hydrochloric acid (32%) (8.0 mL) was added (pH < 1). The yellow precipitate formed was collected by suction filtration, washed with cold (0 °C) water (20 mL), and dried in vacuo over P_2O_5 at room temp. to yield 5.67 g (22.5 mmol, 71%) of yellow crystals; m.p. 237−238 °C (decomposition). − IR (KBr): $\tilde{\nu}$ = 3510, 3360, 3240, 2400, 1890, 1640, 1585, 1460, 1435, 1395, 1195, 1135, 1075, 985, 850, 615 cm^{-1}.

3,6-Bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazine (3): Warning! BTT (**3**) and even its dihydro derivative **2** should only be used in small quantities with all possible precautions (safety goggles, safety mask, leather gloves, leather apron, explosive protection screen). The dihydro tetrazine can be stored in a dry state in a refrigerator. Larger amounts of BTT (> 200 mg) should never be stored in a dry state. We usually divided BTT into small portions, which were dried almost immediately prior to use. Never heat or scratch samples of BTT; exposure of the crystalline BTT to electrostatic charge should also be strictly avoided!

CrO_3 (31.2 g, 313 mmol) was dissolved in a mixture of concentrated sulfuric acid (97%) (31.3 mL) and water (313 mL) at −10 °C. After the addition of 3,6-bis(tetrazol-5-yl)-1,4-dihydro-1,2,4,5-tetrazine dihydrate (**2**) (5.67 g, 22.5 mmol), the mixture was stirred at −5 °C for 0.5 h. The colour of the reaction mixture turned red and a carmine-red precipitate was formed. This precipitate was collected by suction filtration, washed with a mixture of concentrated hydrochloric acid and water (1:10; 15 mL), divided into small portions (< 200 mg), and dried in vacuo over P_2O_5 at room temp. to yield 3.52 g (16.1 mmol, 72%) of carmine-red needles; m.p. 220 °C (violent explosive decomposition). − IR (KBr): $\tilde{\nu}$ = 3300−2300 (br), 1545, 1455, 1440, 1420, 1270, 1240, 1080, 1050, 1040, 1020, 915 cm^{-1}. − $C_4H_2N_{12}$ (218.2): calcd. C 22.02, H 0.92, N 77.16; found C 21.98, H 1.17, N 75.0.

1,4-Bis(2*H*-tetrazol-5-yl)-6,7-dihydro-5*H*-cyclopenta[*d*]pyridazine (5): Caution! BTT (**3**) (500 mg, 2.29 mmol) was suspended in absolute acetonitrile (10 mL). A solution of 1-methoxycyclopentene (340 mg, 3.44 mmol) in absolute acetonitrile (10 mL) was then rapidly added under nitrogen atmosphere. The red colour of the solution disappeared after stirring at room temp. for 10 days. The solvent was then removed and the residue was recrystallized from ethyl acetate to yield 550 mg (2.15 mmol, 95%) of colourless crystals of **5**; m.p. > 280 °C. − IR (KBr): $\tilde{\nu}$ = 3300−2400, 1595, 1585, 1550, 1540, 1510, 1470, 1430, 1410, 1360, 1300, 1270, 1230, 1190, 1165, 1145, 1120, 1090, 1060, 1040, 940, 920, 775 cm^{-1}. − ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ = 2.19−2.32 (m, 2 H), 3.49 (t, 4 H, *J* = 7.7 Hz), 14.0 (br. s, 2 H). − EI MS (70 eV): *m*/*z* (%) = 256 (8) [M$^+$], 228 (15) [M$^+$ − N$_2$], 214 (21), 199 (21) [M$^+$ − tetrazolyl], 186 (22), 171 (21), 160 (24), 143 (47) [5,6,7-trihydropyridazine$^+$], 115 (95) [5,6,7-trihydropyridazine$^+$ − N$_2$]. − $C_9H_8N_{10}$ (256.0): calcd. C 42.19, H 3.15, N 54.66; found C 42.32, H 3.33, N 54.35.

1,4-Bis(2*H*-tetrazol-5-yl)-5,6,7,8,9,10-hexahydrocycloocta[*d*]-pyridazine (6): Caution! BTT (**3**) (100 mg, 0.46 mmol) was suspended in absolute acetonitrile (10 mL). A solution of cyclooctyne (61.0 mg, 0.57 mmol) in absolute acetonitrile (5.0 mL) was then rapidly added under nitrogen atmosphere. The red colour of the solution disappeared after stirring at room temp. for 5 min. The solvent was then removed, the residue was redissolved in absolute acetonitrile (70 mL), and this solution was filtered. Removal of one-third of the solvent led to the deposition of 113 mg (0.38 mmol, 83%) of colourless crystals of **6**; m.p. 280 °C (violent decomposition). − IR (KBr): $\tilde{\nu}$ = 3270, 2940, 2860, 1530, 1515, 1480, 1450, 1400, 1360, 1300, 1210, 1180, 1140, 1100, 1080, 1065, 1010, 950, 890, 870, 790, 760, 700, 660, 610 cm^{-1}. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.40 (br. s, 4 H), 1.88 (br. s, 4 H),

3.25−3.55 (m, 4 H), 7.58 (br. s, 2 H). − UV/vis (CH_3CN): λ_{max} (ε) = 226 (24300), 260 nm (15800). − EI MS (70 eV): *m/z* (%) = 242 (14) [$M^+ - 2N_2$], 213 (50), 185 (26), 171 (23), 129 (26), 107 (46), 43 (75), 41 (100) [$NCNH^+$]. − $C_{12}H_{14}N_{10}$ (298.3): calcd. C 48.31, H 4.73, N 46.95; found C 48.06, H 4.94, N 46.73.

5-Octylfuran-2-carboxylic Acid: A solution of *n*-butyllithium in *n*-hexane (1.6 M, 150 mL, 0.24 mol) was dropped into a solution of 2-octylfuran[33] (19.7 g, 0.11 mol) in absolute tetrahydrofuran (100 mL) at −40 °C over a period of 0.5 h under argon atmosphere. After stirring at this temperature for 4 h, the reaction mixture was poured into a suspension of finely crushed solid carbon dioxide in absolute diethyl ether (100 mL). After all the carbon dioxide had evaporated, the solution was extracted with water (4 × 100 mL). The aqueous phase was washed with diethyl ether (2 × 50 mL) and hydrolyzed with hydrochloric acid (32%) (40 mL). Extraction of the aqueous solution with diethyl ether (2 × 100 mL), drying of the organic phase with Na_2SO_4, and removal of the solvent yielded crude 5-octylfuran-2-carboxylic acid. Two recrystallizations from 40/60 petroleum ether yielded 4.09 g (18.2 mmol, 17%) of pure 5-octylfuran-2-carboxylic acid as colourless crystals; m.p. 71−72 °C. − IR (KBr): $\tilde{\nu}$ = 3300−2400, 3150, 2980, 2920, 2860, 2680, 2590, 1670, 1595, 1530, 1520, 1465, 1425, 1310, 1210, 1165, 1020, 800, 760 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 3 H, *J* = 6.5 Hz), 1.15−1.45 (m, 10 H), 1.63−1.75 (m, 2 H), 2.71 (t, 2 H, *J* = 7.7 Hz), 6.17 (d, 1 H, *J* = 3.4 Hz), 7.25 (d, 1 H, *J* = 3.4 Hz). − EI MS (70 eV): *m/z* (%) = 224 (52) [M^+], 179 (47) [$M^+ - CO_2H$], 139 (24), 138 (15), 136 (14), 126 (83) [$M^+ - C_7H_{14}$], 125 (100) [$M^+ - C_7H_{15}$], 123 (212), 121 (11), 113 (11), 112 (12), 97 (10), 95 (14), 82 (19), 81 (59) [$M^+ - CO_2H - C_7H_{14}$], 79 (16), 67 (15) [$C_4H_3O^+$], 57 (32), 55 (19), 43 (29), 41 (25). − $C_{13}H_{20}O_3$ (224.3): calcd. C 69.61, H 8.99; found C 69.40, H 8.77.

5-Octylfuran-2-carboxylic Acid Chloride (11h): A mixture of 5-octylfuran-2-carboxylic acid (4.45 g, 35.9 mmol) and thionyl chloride (5.22 mL, 8.54 g, 71.8 mmol) was heated under reflux for 1 h under argon atmosphere. After removal of the excess thionyl chloride, the residue was fractionally distilled under reduced pressure to yield 5.41 g (34.1 mmol, 95%) of **11h** as a colourless liquid; b.p. 53−55 °C/0.1 Torr, n_D^{20} = 1.530. − IR (film): $\tilde{\nu}$ = 3150, 3120, 2980, 2940, 2880, 1735, 1565, 1495, 1250, 1020, 970, 810, 670 cm^{-1}.

General Procedure for the Reaction of BTT (3) with Acylating Agents: A mixture of BTT (**3**) and the acylating agent was heated under argon atmosphere. Subsequently, the solvent was removed or the precipitate formed after cooling was collected by suction filtration and the residue was purified as described.

3,6-Bis[5-(*N*-phenylamino)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (7): Caution! Following the general procedure, BTT (**3**) (147 mg, 0.67 mmol) and phenyl isocyanate (5.45 g, 45.8 mmol) yielded, after heating at 165−175 °C for 45 min., removal of the solvent, and recrystallization of the crude product from *N*,*N*-dimethylformamide, 176 mg (0.44 mmol, 75%) of **7** as orange crystals; m.p. 289−295 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3260, 3050, 1630, 1580, 1500, 1455, 1390, 1250, 1160, 1090, 1050, 1040, 750, 690 cm^{-1}. − ^1H NMR ([D_6]DMSO, 250 MHz): δ = 7.08−7.14 (m, 2 H), 7.41−7.47 (m, 4 H), 7.67−7.71 (m, 4 H), 11.36 (s, 1 H). − FD MS (DMF): *m/z* (%) = 400 (0.5) [M^+], 186 (100) [2-*N*-phenylamino-5-cyano-1,3,4-oxadiazole$^+$], 120 (91) [$PhNHCO^+$], 92 (26) [$PhNH^+$], 77 (71) [Ph^+], 65 (19), 51 (26), 39 (15). − $C_{18}H_{12}N_{10}O_2$ (400.4): calcd. C 53.99, H 3.03, N 34.99; found C 53.69, H 4.16, N 34.91.

3,6-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazine (12a): Caution! Following the general procedure, BTT (**3**) (40.0 mg, 0.18 mmol) and benzoyl chloride (**11a**) (2.42 g, 17.2 mmol) yielded, after heating at 150−155 °C for 30 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with dry benzene (5 mL), 57.0 mg (0.15 mmol, 83%) of **12a** as red crystals; m.p. > 280 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3060, 1600, 1565, 1540, 1480, 1455, 1310, 1280, 1175, 1100, 1080, 1030, 1000, 970, 930, 790, 730, 710, 700 cm^{-1}. − ^1H NMR ([D_6]DMSO, 250 MHz): δ = 7.65−7.78 (m, 6 H), 8.09−8.27 (m, 4 H). − UV/vis (CH_3CN): λ_{max} (ε) = 508 nm (487). − $E_{1/2}$ = −0.79 V. − EI MS (70 eV): *m/z* (%) = 372 (16) [M^+ + 2H], 370 (10) [M^+], 172 (32), 171 (55), 115 (100), 77 (67) [Ph^+]. − $C_{18}H_{10}N_8O_2$ (370.3): calcd. C 58.37, H 2.72, N 30.26; found C 58.14, H 2.85, N 30.18.

3,6-Bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (12b): Caution! Following the general procedure, BTT (**3**) (200 mg, 0.92 mmol) and 4-*tert*-butylbenzoyl chloride (**11b**) (5.03 g, 25.6 mmol) yielded, after heating at 165−175 °C for 100 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with acetonitrile (5 mL), 328 mg (0.68 mmol, 74%) of **12b** as red plates; m.p. 265−267 °C. − IR (KBr): $\tilde{\nu}$ = 2970, 1610, 1560, 1540, 1485, 1430, 1170, 1110, 1085, 1040, 1000, 840 cm^{-1}. − ^1H NMR ([D_6]DMSO, 250 MHz): δ = 1.37 (s, 18 H), 7.73−7.77 (m, 4 H), 8.16−8.19 (m, 4 H). − UV/vis (CH_3CN): λ_{max} (ε) = 200 (44700), 248 (31800), 344 (34900), 513 nm (509). − $E_{1/2}$ = −0.74 V. − FD MS (DMF): *m/z* (%) = 482 (100) [M^+]. − $C_{26}H_{26}N_8O_2$ (482.6): calcd. C 64.70, H 5.44, N 23.22; found C 64.46, H 5.45, N 23.10.

3,6-Bis[5-(4-octylphenyl)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (12c): Caution! Following the general procedure, BTT (**3**) (188 mg, 0.86 mmol) and 4-octylbenzoyl chloride (**11c**)[29] (4.00 g, 15.8 mmol) yielded, after heating at 163 °C for 60 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with *n*-pentane (20 mL), 266 mg (0.45 mmol, 52%) of **12c** as red plates; m.p. 182−184 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 3070, 3030, 2960, 2940, 2860, 1605, 1560, 1545, 1480, 1465, 1435, 1170, 1110, 1090, 1020, 1010, 960, 920, 875, 860, 740 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, 6 H, *J* = 6.6 Hz), 1.28−1.34 (m, 20 H), 1.62−1.71 (m, 4 H), 2.73 (t, 4 H, *J* = 7.7 Hz), 7.39−7.44 (m, 4 H), 8.19−8.24 (m, 4 H). − UV/vis (CH_2Cl_2): λ_{max} (ε) = 252 (31800), 361 (31400), 523 nm (550). − $E_{1/2}$ = −0.74 V. − FD MS (CH_2Cl_2): *m/z* (%) = 594 (100) [M^+], 297.3 (15) [M^{2+}]. − $C_{34}H_{42}N_8O_2$ (594.8): calcd. C 68.66, H 7.12, N 18.84; found C 68.77, H 7.12, N 18.91.

3,6-Bis[5-(4-heptyloxyphenyl)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (12d): Caution! Following the general procedure, BTT (**3**) (198 mg, 0.91 mmol) and 4-heptyloxybenzoyl chloride (**11d**) (4.72 g, 18.5 mmol) yielded, after heating at 160 °C for 120 min., cooling to room temp., collection of the precipitate by suction filtration, washing with *n*-pentane (20 mL), and recrystallization from CH_2Cl_2, 428 mg (0.72 mmol, 77%) of **12d** as orange needles; m.p. 238−242 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3100, 3080, 2960, 2940, 2830, 1600, 1560, 1475, 1460, 1430, 1300, 1280, 1250, 1160, 1090, 1015, 960, 920, 850 cm^{-1}. − ^1H NMR ([D_7]DMF, 250 MHz): δ = 0.91 (t, 6 H, *J* = 6.6 Hz), 1.26−1.49 (m, 16 H), 1.79−1.90 (m, 4 H), 4.09 (t, 4 H, *J* = 6.6 Hz), 7.08−7.14 (m, 4 H), 8.20−8.26 (m, 4 H). − UV/vis (CH_2Cl_2): λ_{max} (ε) = 269 (42900), 389 (33600), 523 nm (620). − $E_{1/2}$ = −0.76 V. − FD MS (CH_2Cl_2): *m/z* (%) = 598 (100) [M^+]. − $C_{32}H_{38}N_8O_4$ (598.7): calcd. C 64.19, H 6.40, N 18.72; found C 64.36, H 6.42, N 18.76.

3,6-Bis[5-(4-octadecylphenyl)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (12e): Caution! Following the general procedure, BTT (**3**) (100 mg, 0.46 mmol) and 4-octadecylbenzoyl chloride (**11e**) (2.10 g, 5.34 mmol) yielded, after heating at 170 °C for 120 min., cooling

to room temp., collection of the precipitate by suction filtration, washing with *n*-pentane (30 mL) and CH_2Cl_2 (40 mL), and recrystallization from CH_2Cl_2, 73.1 mg (0.084 mmol, 18%) of **12e** as red needles; m.p. 144−146 °C. − IR (KBr): $\tilde{\nu}$ = 3050, 2940, 2910, 2840, 1600, 1555, 1540, 1475, 1455, 1425, 1155, 1075, 1005, 945, 845 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 6 H, *J* = 6.6 Hz), 1.13−1.46 (m, 60 H), 1.61−1.81 (m, 4 H), 2.73 (t, 4 H, *J* = 7.7 Hz), 7.39−7.46 (m, 4 H), 8.19−8.26 (m, 4 H). − UV/vis ($CHCl_3$): λ_{max} (ε) = 264 (33900), 375 (30900), 535 nm (590). − $E_{1/2}$ not determined due to insufficient solubility. − FD MS ($CHCl_3$): *m*/*z* (%) = 876 (100) [M^+ + 2H], 875 (80) [M^+ + H]. − $C_{54}H_{82}N_8O_2$ (875.3): calcd. C 74.10, H 9.44, N 12.81; found C 73.16, H 9.49, N 12.64.

3,6-Bis[5-(thiophen-2-yl)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (12f): Caution! Following the general procedure, BTT (**3**) (100 mg, 0.46 mmol) and thiophene-2-carbonyl chloride (**11f**) (8.23 g, 56.2 mmol) yielded, after heating at 140−155 °C for 45 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with dry benzene (30 mL), 131 mg (0.34 mmol, 74%) of **12f** as red crystals; m.p. 278−280 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 1575, 1565, 1500, 1490, 1480, 1430, 1410, 1315, 1300, 1280, 1210, 1165, 1080, 1040, 1020, 990, 940, 920, 850, 750, 730 cm^{-1}. − ^1H NMR ([D_6]DMSO, 250 MHz): δ = 7.42 (dd, 2 H, *J* = 4.0 Hz), 8.15 (d, 4 H, *J* = 4.0 Hz). − UV/vis (CH_3CN): λ_{max} (ε) = 506 nm (101). − $E_{1/2}$ = −0.74 V. − EI MS (70 eV): *m*/*z* (%) = 382 (11) [M^+], 177 (55), 121 (41), 111 (100), 95 (16), 69 (35). − $C_{14}H_6N_8O_2S_2$ (382.4): calcd. C 43.97, H 1.58, N 29.30; found C 44.06, H 1.84, N 28.84.

3,6-Bis[5-(5-octylthiophen-2-yl)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (12g): Caution! Following the general procedure, BTT (**3**) (108 mg, 0.49 mmol) and 5-octylthiophene-2-carbonyl chloride (**11g**) (2.00 g, 7.73 mmol) yielded, after heating at 155 °C for 165 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with *n*-pentane (20 mL), 120 mg (0.20 mmol, 41%) of **13g** as red plates; m.p. 177−179 °C. − IR (KBr): $\tilde{\nu}$ = 3100, 2960, 2930, 2860, 1575, 1560, 1495, 1465, 1455, 1425, 1310, 1165, 1075, 1050, 1030, 995, 820, 735 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, 6 H, *J* = 6.0 Hz), 1.29−1.50 (m, 20 H), 1.70−1.83 (m, 4 H), 2.93 (t, 4 H, *J* = 7.6 Hz), 6.96 (d, 2 H, *J* = 3.8 Hz), 7.90 (d, 2 H, *J* = 3.8 Hz). − UV/vis (CH_2Cl_2): λ_{max} (ε) = 280 (24300), 399 (33300), 522 nm (590). − $E_{1/2}$ = −0.74 V. − FD MS ($CHCl_3$): *m*/*z* (%) = 606 (100) [M^+]. − $C_{30}H_{38}N_8O_2S_2$ (606.8): calcd. C 59.38, H 6.31, N 18.47; found C 59.36, H 6.43, N 18.69.

3,6-Bis[5-(5-octylfuran-2-yl)-1,3,4-oxadiazol-2-yl]-1,2,4,5-tetrazine (12h): Caution! Following the general procedure, BTT (**3**) (327 mg, 1.50 mmol) and 5-octylfuran-2-carbonyl chloride (**11h**) (1.90 g, 7.83 mmol) yielded, after heating at 165 °C for 300 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with *n*-pentane (20 mL), 100 mg (0.16 mmol, 11%) of **12h** as red crystals; m.p. 162−164 °C. − IR (KBr): $\tilde{\nu}$ = 3120, 2940, 2920, 2840, 1610, 1535, 1460, 1445, 1375, 1305, 1290, 1120, 1100, 1025, 970, 950, 820, 725 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, 6 H, *J* = 6.6 Hz), 1.20−1.50 (m, 20 H), 1.70−1.90 (m, 4 H), 2.81 (t, 4 H, *J* = 7.6 Hz), 6.33 (d, 2 H, *J* = 3.6 Hz), 7.43 (d, 2 H, *J* = 3.6 Hz). − UV/vis (CH_2Cl_2): λ_{max} (ε) = 275 (42600), 402 (27000), 520 nm (615). − $E_{1/2}$ = −0.73 V. − FD MS ($CHCl_3$): *m*/*z* (%) = 575 (100) [M^+]. − $C_{30}H_{38}N_8O_4$ (574.7): calcd. C 62.69, H 6.66, N 19.50; found C 62.79, H 6.36, N 19.31.

3,6-Bis(5-methyl-1,3,4-oxadiazol-2-yl)-1,2,4,5-tetrazine (12i): Caution! Following the general procedure, BTT (**3**) (147 mg, 0.67 mmol) and acetic anhydride (5.43 g, 53.2 mmol) yielded, after heating at 130 °C for 150 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with cyclohexane (5 mL), 135 mg (0.55 mmol, 82%) of **12i** as red crystals; m.p. 243−245 °C. − IR (KBr): $\tilde{\nu}$ = 3140, 3040−2900, 1460, 1430, 1375, 1175, 1050, 1000, 965, 930, 710 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.84 (s, 6 H). − UV/vis (CH_3CN): λ_{max} (ε) = 524 nm (528). − $E_{1/2}$ = −0.77 V. − EI MS (70 eV): *m*/*z* (%) = 246 (8) [M^+], 109 (21), 53 (11), 43 (100) [CH_3CO^+]. − $C_8H_6N_8O_2$ (246.0): calcd. C 39.03, H 2.46, N 45.52; found C 39.22, H 2.63, N 45.16.

3,6-Bis(*N*-acetyltetrazol-5-yl)-1,2,4,5-tetrazine (13): Caution! Following the general procedure, BTT (**3**) (151 mg, 0.69 mmol) and acetyl chloride **(11i)** (4.42 g, 56.3 mmol) yielded, after heating under reflux for 120 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with *n*-pentane (5 mL), 173 mg (0.57 mmol, 83%) of **13** as orange crystals, m.p. > 185 °C (decomp.) − IR (KBr): $\tilde{\nu}$ = 2940, 1790, 1410, 1370, 1305, 1280, 1250, 1200, 1165, 1080, 1040, 1000, 955, 910, 640 cm^{-1}. − $C_8H_6N_{12}O_2$ (302.3): calcd. C 31.79, H 2.00, N 55.62; found C 30.91, H 2.39, N 55.58.

Heating of **13** (81.6 mg, 0.27 mmol) in dry 1,2-dichlorobenzene at 170 °C for 180 min., cooling to ambient temperature, collection of the precipitate by suction filtration, and washing with *n*-pentane (5 mL) furnished 58.0 mg (0.24 mmol, 87%) of red crystals; m.p. 242−245 °C. The product was identified as **12i** by comparison of IR data.

General Procedure for the Reaction of BTB (4) with Acylating Agents: A mixture of BTB (**4**) and the acylating agent **11** was heated at 100 °C in dry pyridine under argon atmosphere. Subsequently, the solvent was removed or, after cooling, the precipitate formed was collected by suction filtration and the residue was purified as described.

1,4-Bis[5-(4-octadecylphenyl)-1,3,4-oxadiazol-2-yl]benzene (14a): Following the general procedure, BTB (**4**) (214 mg, 1.00 mmol) and 4-octadecylbenzoyl chloride (**11e**) (2.00 g, 5.09 mmol) yielded, after heating at 100 °C in dry pyridine (5 mL) for 45 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with CH_2Cl_2 (50 mL), 747 mg (0.86 mmol, 86%) of **14a** as colourless crystals; m.p. 210−214 °C. − IR (KBr): $\tilde{\nu}$ = 3080, 2950, 2910, 2830, 1600, 1570, 1560, 1480, 1455, 1065, 1000, 945, 835, 820, 800 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 6 H, *J* = 6.5 Hz), 1.20−1.45 (m, 64 H), 2.71 (t, 4 H, *J* = 7.7 Hz), 7.34−7.40 (m, 4 H), 8.05−8.11 (m, 4 H), 8.32 (s, 4 H). − UV/vis ($CHCl_3$): λ_{max} (ε) = 257 (15900), 329 (45000), 339 nm (45000). − FD MS ($CHCl_3$): *m*/*z* (%) = 871 (100) [M^+], 436 (80) [M^{2+}]. − $C_{58}H_{86}N_4O_2$ (871.3): calcd. C 79.95, H 9.95, N 6.43; found C 79.99, H 9.88, N 6.39.

1,4-Bis(5-cyclohexyl-1,3,4-oxadiazol-2-yl)benzene (14b): Following the general procedure, BTB (**4**) (321 mg, 1.50 mmol) and cyclohexanecarbonyl chloride (**11j**) (1.12 g, 7.65 mmol) yielded, after heating at 100 °C in dry pyridine (15 mL) for 240 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with *n*-pentane (25 mL), 124 mg (0.33 mmol, 22%) of **14b** as colourless crystals; m.p. 209−211 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3090, 2970, 2920, 2850, 1570, 1540, 1490, 1475, 1275, 1200, 1080, 1075, 1000, 950, 840 cm^{-1}. − ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24−1.97 (m, 16 H), 2.10−2.23 (m, 4 H), 3.02 (ddt, 2 H, *J* = 11.2 Hz, *J* = 11.2, *J* = 3.6 Hz), 8.17 (s, 4 H). − UV/vis ($CHCl_3$): λ_{max} (ε) = 296 (35100), 304 (35400), 318 nm (sh, 20400). − EI MS (70 eV): *m*/*z* (%) = 378 (17) [M^+], 323 (25) [$M^+ - C_4H_7$], 310 (100)

$[M^+ - C_5H_8]$, 83 (11) $[C_6H_{11}^+]$, 55 (16) $[C_4H_7^+]$, 41 (7) $[C_3H_5^+]$. − $C_{22}H_{26}N_4O_2$ (378.5): calcd. C 69.81, H 6.93, N 14.81; found C 69.51, H 7.12, N 14.74.

1,4-Bis[5-(5-ethylthiophen-2-yl)-1,3,4-oxadiazol-2-yl]benzene (14c): Following the general procedure, BTB (**4**) (643 mg, 3.00 mmol) and 5-ethylthiophene-2-carbonyl chloride (**11k**) (2.45 g, 14.0 mmol) yielded, after heating at 100 °C in dry pyridine (15 mL) for 30 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with *n*-pentane (20 mL), 1.17 g (2.69 mmol, 90%) of **14c** as colourless crystals; m.p. 238−239 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3080, 3060, 2960, 2920, 2860, 1575, 1560, 1505, 1475, 1440, 1400, 1070, 1060, 1040, 1015, 1005, 950, 810, 795, 710 cm^{-1}. − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 1.38 (t, 6 H, *J* = 7.5 Hz), 2.95 (dq, 4 H, *J* = 7.5 Hz, *J* = 1.0 Hz), 6.94 (dt, 2 H, *J* = 3.8 Hz, *J* = 1.0 Hz), 7.69 (d, 2 H, *J* = 3.8 Hz), 8.26 (s, 4 H). − UV/vis (CH_3CN): λ_{max} (ε) = 226 (5900), 256 (5700), 343 nm (21500). − EI MS (70 eV): *m*/*z* (%) = 434 (78) $[M^+]$, 283 (32) $[M^+ - (H_5C_2-C_4H_2S-CN_2)]$, 281 (3) $[M^+ - (H_5C_2-C_4H_2S-CNO)]$, 227 (27), 184 (6), 139 (100) $[H_5C_2-C_4H_2S-CO^+]$, 122 (5). − $C_{22}H_{18}N_4O_2S_2$ (434.5): calcd. C 60.81, H 4.18, N 12.90; found C 60.91, H 4.25, N 12.92.

1,4-Bis[5-(furan-2-yl)-1,3,4-oxadiazol-2-yl]benzene (14d): Following the general procedure, BTB (**4**) (643 mg, 3.00 mmol) and furan-2-carbonyl chloride (**11l**) (1.83 g, 14.0 mmol) yielded, after heating at 100 °C in dry pyridine (15 mL) for 30 min., cooling to room temp., collection of the precipitate by suction filtration, and washing with *n*-pentane (20 mL), 0.90 g (2.60 mmol, 87%) of **14d** as colourless crystals; m.p. 249−253 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3120, 1615, 1560, 1505, 1480, 1470, 1440, 1430, 1400, 1160, 1095, 1075, 1005, 990, 960, 885, 820, 760, 750, 715, 680 cm^{-1}. − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 6.69 (dd, 2 H, *J* = 3.6 Hz, *J* = 1.8 Hz), 7.30 (dd, 2 H, *J* = 3.6 Hz, *J* = 0.8 Hz), 7.74 (dd, 2 H, *J* = 1.8 Hz, *J* = 0.8 Hz), 8.30 (s, 4 H). − UV/vis (CH_2Cl_2): λ_{max} (ε) = 252 (16800), 326 (43400), 335 nm (44000). − EI MS (70 eV): *m*/*z* (%) = 346 (100) $[M^+]$, 239 (66) $[M^+ - (C_4H_3O-CN_2)]$, 237 (5) $[M^+ - (C_4H_3O-CNO)]$, 183 (34), 130 (5), 118 (5), 104 (6), 95 (67) $[C_4H_3O-CO^+]$, 122 (5). − $C_{18}H_{10}N_4O_4$ (346.3): calcd. C 62.43, H 2.91, N 16.18; found C 62.47, H 2.95, N 16.18.

1,4-Bis[5-(*N*-methylpyrrol-2-yl)-1,3,4-oxadiazol-2-yl]benzene (14e): Following the general procedure, BTB (**4**) (643 mg, 3.00 mmol) and *N*-methylpyrrole-2-carbonyl chloride (**11m**) (2.01 g, 14.0 mmol) yielded, after heating at 100 °C in dry pyridine (15 mL) for 60 min., cooling to room temp., collection of the precipitate by suction filtration, washing with *n*-pentane (20 mL), and recrystallization from CH_3CN, 0.81 g (2.18 mmol, 73%) of **14e** as colourless crystals; m.p. 264−266 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3110, 2995, 2950, 1590, 1570, 1500, 1480, 1460, 1400, 1095, 1070, 1050, 1005, 955, 840, 715, 685 cm^{-1}. − ^1H NMR (CD_2Cl_2, 250 MHz): δ = 4.09 (s, 6 H), 6.28 (dd, 2 H, *J* = 4.0 Hz, *J* = 2.6 Hz), 6.91−6.94 (m, 2 H), 7.00 (dd, 2 H, *J* = 4.0 Hz, *J* = 1.8 Hz), 8.25 (s, 4 H). − UV/vis (CH_2Cl_2): λ_{max} (ε) = 266 (35600), 353 nm (41100). − EI MS (70 eV): *m*/*z* (%) = 372 (100) $[M^+]$, 315 (12), 252 (37) $[M^+ - (C_4H_3NCH_3-CN_2)]$, 250 (8) $[M^+ - (C_4H_3NCH_3-CNO)]$, 224 (4), 196 (5), 186 (6) 168 (25), 108 (71) $[C_4H_3NCH_3-CO^+]$ 106 (14), 90 (7), 65 (6), 53 (9), 39 (7). − $C_{20}H_{16}N_6O_2$ (372.4): calcd. C 64.50, H 4.33, N 22.57; found C 64.41, H 4.36, N 22.32.

3,6-Bis[5-(4-octadecylphenyl)-1,3,4-oxadiazol-2-yl]pyridazine (15): A mixture of **12e** (81.5 mg, 0.093 mmol) and norborna-2,5-diene (85.8 mg, 931 μmol) in 40 mL of dry CH_2Cl_2 was stirred at room temp. After 180 min., the red colour of the suspension had faded. After evaporation of the solvent, recrystallization of the residue from CH_2Cl_2/methanol (1:4) yielded 62.2 mg (0.071 mmol, 77%) of **15** as colourless crystals, m.p. 168−170 °C (decomp.). − IR (KBr): $\tilde{\nu}$ = 3040, 2950, 2910, 2840, 1475, 1465, 1425, 1075, 1015, 960, 850, 720 cm^{-1}. − ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (t, 6 H, *J* = 7.0 Hz), 1.20−1.45 (m, 60 H), 1.65−1.87 (m, 4 H), 2.72 (t, 4 H, *J* = 7.7 Hz), 7.37−7.42 (m, 4 H), 8.16−8.21 (m, 4 H), 8.32 (s, 2 H). − UV/vis ($CHCl_3$): λ_{max} (ε) = 252 (25000), 335 nm (37800). − EI MS (70 eV): *m*/*z* (%) = 873 (53) $[M^+]$, 355 (61) $[H_{41}C_{24}CN^+]$, 326 (36), 312 (50), 298 (44), 285 (53), 271 (59), 257 (53), 130 (55), 116 (62), 57 (67), 43 (100) $[C_3H_7^+]$. − $C_{56}H_{84}N_6O_2$ (873.3): calcd. C 77.02, H 9.70, N 9.63; found C 76.57, H 9.40, N 9.66.

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